Determining Ice Content of a Fine Ice Slurry from Density Measurements

L. C. Dickey
E. R. Radewonuk
M. F. Dallmer
U.S. Department of Agriculture
Agricultural Research Service
Eastern Regional Research Center
Philadelphia, PA 19118

Concentration of aqueous solutions by ice formation and removal has attractive features that motivated the development of several commercial processes. One subset of these freeze concentration processes is based on the contention that the particles must grow to around 300 μm dia. to obtain clean separation of the ice from the concentrate (Omran, 1974). The increased residence time required to grow large ice crystals is a penalty which increases in severity as the plant size decreases. We have been investigating a short residence time, evaporatively chilled process for concentrating milk which we think will have a relatively low capital cost. Efficient separation of fine ice particles will be crucial to the commercial feasibility of the process, and to evaluate the separation, an accurate method of measuring the ice content of a fine particle slurry is needed.

Determining the ice content of a slurry of fine particles (frazil ice) by sample filtration is complicated by melting of the finest particles during the sampling and filtration process. A fluid property of the sample (in addition to mass) must be measured before and after separation of the ice to determine the amount of this melting. The liquid-phase concentration of an ice slurry can be based on the slurry pressure or temperature if it is at equilibrium (and the triple point values of temperature or pressure as a function of composition are known). But for some, if not all freeze concentratable feeds processes, triple-point data for the mixtures involved are not available. Also, the processes are not at equilibrium. In addition to its use in characterizing the feed to the ice separation equipment, an accurate ice content determination can be used to relate supercooling and freezing rate.

In many cases, continuously and immediately frozen slurries that have not been recirculated in a growth tank will not have a liquid phase of uniform concentration (Bomben, 1987; Levin, 1981). Consequently, a layer of liquid of higher-than-bulk solute content will cling to the ice particles after filtrate drainage.

Only an *in situ* method of ice content determination can give a sure measure of this effect since detection of possible enhanced concentration of the liquid retained on the ice after filtration is confounded by possible melting during filtration.

Basis of Method

We have found that ice content can be determined simply by use of on-line density measurements of the slurry along with measurements of the melted slurry at (or near) its melting temperature.

Equation 1 defines slurry specific volume based on adding the volumes of the solid and liquid phases in the slurry. It is based on the assumption that each phase is homogeneous and that the solid contains no solute.

$$[x/sg_{ice}] + [(1 - x)/sg_{liq}] = 1/sg_{slurry} \qquad (1)$$

where

sg_{ice} = specific gravity of ice
sg_{liq} = specific gravity of the liquid phase
        originally present in the slurry
  x = ice content in weight fraction

Inspection of Eq. 1 shows that we need only determine the densities of the slurry and the liquid phase to determine x, since the density of ice and the density of pure water at any temperature (for converting density to specific gravity) are known. The slurry density can be determined reasonably accurately with a flow-through, vibrating tube type instrument (Picker, 1974). After the slurry density has been measured, the fluid in a loop including the density measuring instrument can be trapped by valve switching, recirculated with heating until it melts, and the melted slurry density identified with the density when the fluid begins to exceed the original melting temperature.

One way to extract the original liquid specific gravity (the product of a hypothetical perfect filtration, with no ice melting), for use in Eq. 1, from the measurement of melted slurry density is to determine the relation between the solute weight fraction, w, and the specific gravity of the solution in question, at its melting temperature.

Assume that the desired relation is given by Eq. 2:

$$sg_m = f(w_m) \qquad (2)$$

where the subscript m refers to the melted slurry at its melting temperature.

In principle, an inverse function exists, allowing weight fraction values to be derived from specific gravity:

$$w_m = f'(sg_m) \qquad (3)$$

Using these expressions, the liquid weight fraction, w_{liq}, and specific gravity, sg_{liq}, can be related to the melted-slurry weight fraction and density:

$$w_{liq} = w_m/(1 - x) = [f'(sg_m)]/(1 - x)$$
$$sg_{liq} = f\{[f'(sg_m)]/(1 - x)\} \qquad (4)$$

sg_{liq} from Eq. 4 can be substituted in Eq. 1 and solved (implicitly) for x.

If the partial molal volume for the hydrated solute is constant, the solution density will be linear in solute concentration (Kiyosawa, 1988):

$$\rho = \rho_{aq} + (MW - \rho_{aq}V^*)c \qquad (5)$$

where

ρ_{aq} = density of water for which we use 1,000 kg/m^3

[since most solutions we are interested in freeze no lower than a few degrees below 0° and supercooled water is 999 or more down to −6° (Kell, 1975).]

MW = solute molecular weight
V^* = partial molal volume of the solute
c = solute molar concentration

and since

$$c = \rho w/MW$$
$$sg = 1 + sg\,w[1 - \rho_{aq}V^*/MW]$$
$$sg = 1/(1 - \alpha w) \qquad (6)$$

where

$$\alpha = 1 - \rho_{aq}V^*/MW$$

Eq. 6 can be substituted in Eq. 4, giving,

$$sg_{liq} = (1 - \alpha w_{liq})^{-1} = \{[(1/sg_m) - x]/(1 - x)\}^{-1} \qquad (7)$$

which, when substituted in Eq. 1, gives, independently of α,

$$(x/sg_{ice}) + [(1/sg_m) - x] = 1/sg_{slurry} \qquad (8)$$

Table 1. α for Freezing Sucrose Solutions

Solute Wt. Fraction w	Sp. Gr. at Freezing	α from Eq. 6
0.005	1.00199	0.3972
0.01	1.00399	0.3974
0.02	1.00801	0.3973
0.04	1.01613	0.3968
0.10	1.04121	0.3958
0.15	1.06297	0.3949
0.20	1.08554	0.3940
0.30	1.13332	0.3921
0.40	1.18499	0.3903

The question remains whether Eq. 6 is sufficiently accurate at the freezing temperature. Unfortunately, density and solute concentrations in ice slurries are not available for many solutes of interest. The required information can be determined for sucrose solutions from the freezing point depression values reported by Weast (1985) and a fourth-order polynomial function for sucrose density, dependent on temperature and concentration (Wagenbreth et al., 1988). From these it is possible to calculate specific gravity at the freezing temperature for various values of w and then calculate the corresponding α from Eq. 6. These are listed in Table 1.

The constancy of the α values in Table 1 justifies the use of Eqs. 6 and 8, at least for sucrose solutions. Using $\alpha = 0.397$, which corresponds to $V^* = 0.206$ dm$^3 \cdot$ mol^{-1}), Eq. 6 fits Wagenbreth's specific gravity correlation within 1.3% up to 0.3 weight fraction sucrose. This value is in agreement with a recently published (Kaulgud, 1988) value, 0.207 dm^3/mol, for the infinitely dilute apparent molal volume. The specific gravity variation of other sugar solutions is comparable (Weast, 1987). Experimentally we find that α for lactose = 0.378, corresponding to $V^* = 0.213$, which does not agree as well with Kaulgud's value of 0.205 at 5°C.

Electrolyte solutions appear to be equally well described by the constant molal volume assumption embodied in Eq. 6. The specific gravity of freezing NaCl solutions can be determined from correlations provided by Chen (1987) and Munson (1980) and are listed in Table 2 along with corresponding values calculated with $\alpha = 0.680$ in Eq. 6.

Millero (1970) reported careful measurements of partial molal volume of NaCl solutions which increase with concentration at 0°. Apparently the drop in freezing temperature counters the concentration effect on density at constant temperature, as shown in Tables 1 and 2. Since no theoretical explanation for this is now available, the validity of the constant molal volume

Table 2. Specific Gravity of Freezing NaCl Solutions

Solute Wt. Fraction, w	Sp. Gr. Pub. Corr.*	Eq. 6**
0.001	1.000679	1.000680
0.01	1.006836	1.006847
0.05	1.035176	1.035197
0.10	1.072934	1.072961
0.20	1.157462	1.157407

*The equation derived from Chen (1987) and Munson (1980) is $sg = 1.0000 + 6.7864 \times 10^{-5}\,w + 0.49382\,w^2 + .015627\,w^3 + 1.16038\,w^4$.
**The value, $\alpha = 0.680$, corresponding to $V^* = 0.0187$ dm$^3 \cdot$ mol^{-1} was used in Eq. 6 to get the best agreement with the values in the second column.
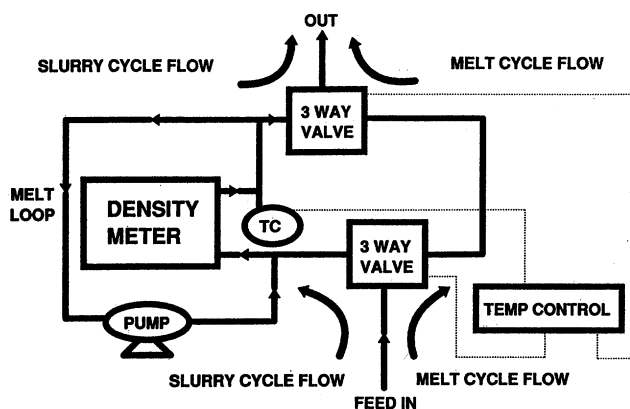
Figure 1. Specific gravity measurement system.

for a given solute would need to be checked over the concentration range of interest.

Experiment

Equipment arranged as shown in Figure 1 was used to measure densities and temperatures of slurries prepared continuously from sucrose solutions using an evaporatively cooled (direct) freezer. A Dynatrol density cell capable of specific gravity measurement in the range 0.7–1.2 was calibrated using methanol-water mixtures for low densities, and saline solutions for high densities. Reference densities for the solutions were taken from *Perry's Handbook* (1984).

Type T thermocouples were used for temperature measurement and control of flow through the loop by activation of electrically operated ball valves through the agency of an Omega CN 9000 series controller as shown in Figure 1. The pump runs continuously to obtain simplicity and reproducibility of operation. After the measured temperature has dropped below the set point by a predetermined amount for a predetermined period, the valves switch position as shown and the slurry feed bypasses the sample loop. The slurry sample recirculates in the loop until the ice melts and the temperature rises to the set point. During a cycle, specific gravity and temperature signals are automatically logged every 20 s.

Typical variation of temperature and specific gravity during a measurement cycle are shown in Figure 2. Flow rate through the freezer during sampling and on-line measurement was 270 kg/h. Slurry samples of two different sizes, around 500 gm and 40 kg, were taken, filtered, and the solute content and weight of filtrate and melted ice measured. In addition, the large sample was collected in a cylinder, compacted, and rinsed. The rinse was tap water at its freezing point driven through the ice bed by nitrogen pressure, in about 1 min. These measurements were used to calculate ice content, assuming no net ice melting and that the liquid remaining on the ice after drainage or filtration has the same composition as the filtrate, and are listed in Table 3 along with ice content as determined from slurry density measurements and Eq. 8.

Discussion

The data shown in Table 3 demonstrate two effects, concentration polarization (CP) and melting, both of which cause
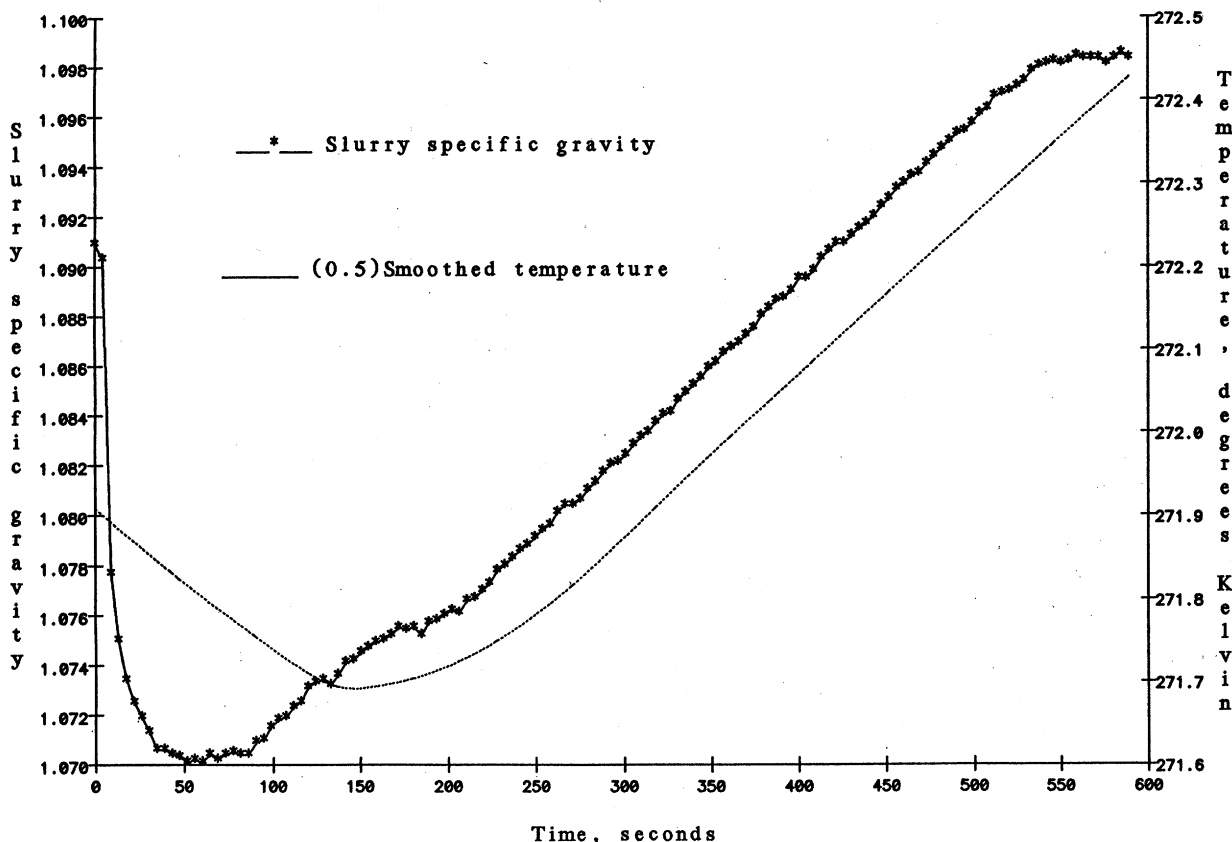

Figure 2. Property variation for a 13 wt. % sucrose slurry sample.

Errata

In a recent R&D note titled "Determining Ice Content of a Fine Ice Slurry from Density Measurements" (Dec. 1989, p. 2033), we used an erroneous equation (footnote to Table 2) which affects the range of validity of the constant molal volume assumption for electrolyte solutions. Therefore, the following corrections are made to the penultimate paragraph, p. 2034 and Table 2:

Electrolyte solutions are *not* well described for solute weight fractions >0.05 by the constant molal volume assumption embodied in Eq. 6. The specific gravity of freezing NaCl solutions can be determined from correlations provided by Chen (1987) and Munson (1980) and are shown in Table 2 (below) along with corresponding values calculated using $\alpha = 0.800$ in Eq. 6.

Millero (1970) reported careful measurements of partial molal volume of NaCl solutions which increase with concentration at 0°C. Apparently the drop in freezing temperature counters most of the effect of concentration on the solution density for freezing solutions since the variation indicated in Table 2 is much less than might be expected from Millero's 0°C data.

Table 2. Specific Gravity of Freezing NaCl Solutions

Wt. Frac. NaCl, w	Solution Sp. Gravity		Difference (Sp. Gr. $-$ 1), %
	Pub. Corr.*	Eq. 6**	
0.001	1.000805	1.000801	0.5
0.01	1.008086	1.008064	0.2
0.05	1.04115	1.04167	1.3
0.10	1.08402	1.08696	3.4
0.20	1.17361	1.19048	9.3

*The equation derived from Chen and Munson is Sp. Gr. $= 1.0000 + 0.80497\, w + 0.36502\, w^2 - 0.015627\, w^3 - 1.16038\, w^4$.

**$\alpha = 0.800$, corresponding to $V^* = 0.0117\ dm^3 \cdot mol^{-1}$, was used in Eq. 6. Millero's infinite dilution NaCl molal volume of $0.0129\ dm^3 \cdot mol^{-1}$ corresponds to $\alpha = 0.780$.

L. C. Dickey
E. R. Radewonuk
M. F. Dallmer
ERRC/ARS USDA
Philadelphia, PA 19118

Table 3. Ice Content Determinations

Method of Determination	Wt. Fraction Ice for Solution with Indicated Solute Avg. Values (No. of Readings)		
	Lactose*	NaCl**	NaCl†
On-Line Density Measurement and Solution for x of Eq. 8	0.274 ± 0.010(5)	0.203 ± 0.004(5)	0.107 ± 0.008(6)
Small Sample Filtration	0.245 ± 0.009(5)	0.200 ± 0.010(4)	0.087 ± 0.0115(3)
Large Sample Filtration	0.232 ± 0.013(3)	—	—
Large Sample Filtr. with Ice Rinse‡	0.221 ± 0.011(2)	0.183 ± 0.013(3)	0.080 ± 0.0003(2)
Min. Slurry Temp., °F(K)	30.7 ± 0.1(272.4)	28.7 ± 0.1(271.3)	21.0 ± 0.1(267.0)

*The liquid-phase component of the slurry was 0.137 ± 0.001.
**The liquid-phase component of the slurry was 0.0328 ± 0.0006.
†The liquid-phase component of the slurry was 0.097 ± 0.001. The density change of a 2 molal NaCl solution due to a 1° temp. rise at the freezing point was 0.3 kg/m^3, corresponding to a 0.0015 weight fraction reduction in the calculated ice content (Kell, 1975). Correction for temperature change during melting was excluded here.
‡3.785 dm^3 of tap water chilled to 273 K used to rinse ice in large sample.

reduction in filtration-based determination of ice content. The difference between the small and large sample determinations for the lactose solution must be due to melting, since CP should be unaffected by sample size or rinsing and there is up to 200 kPa pressure on the ice during collection of the large sample. The rinsed large-sample determination would exceed that of the unrinsed if CP were significant and reducible by rinsing.

Generally, differences between on-line and small sample values must be due to both effects. The close agreement in the case of the .033 weight fraction NaCl solutions (middle column of Table 3) indicates that neither is occurring to a significant extent for these ice slurries. However, for the lactose and more concentrated NaCl solution, although there may be some melting, the major cause of increased apparent ice content difference between the on-line and small samples must be CP. According to the stagnant freezing model of Bomben (1987), increasing solute concentration sharply reduces the thickness of the concentrated solute layer around the ice crystal. A thinner solute layer will be more resistant to solute removal from the ice by drainage and rinsing, resulting in reduced apparent (and for freeze concentration purposes, effective) ice content.

Although developed to determine ice content, the on-line density measurement method could also be used to automatically determine crystal or aggregate content in a process stream if the density change due to aggregation is sufficient and heat-reversible. To obtain more rapid determinations of ice content in freeze concentrations applications, which might be desirable to characterize changes in operating conditions or startup, the automatic aspect of the described method can be sacrificed and slurry samples taken from a point downstream of the density cell for later density measurement and comparison with the corresponding slurry measurements. The correspondence is simple since the delay between the point of on-line measurement and sampling is negligible at usual flow rates (200 kg/h or more).

Acknowledgment

Notation

sg = specific gravity, density of slurry or solution/density of pure water at the same temperature
V^* = partial molal volume
w = weight fraction of solute in liquid
x = weight fraction of ice in a slurry
α = measure of solute effect on solution density at its freezing temperature, defined by Eq. 6
ρ = density

Literature cited

Bomben, J., J. Newman, and C. J. King, "Growth of Radially Symmetric Ice in a Supercooled Sucrose Solution," *Ind. Eng. Chem. Res.*, **26**, 23 (1987).

Chen, C. S., and S. Nagy, "Prediction and Correlation of Freezing Point Depression of Aqueous Solutions," *Trans. ASAE*, **30**, 1176 (1987).

Garrod, J. E., and T. M. Herrington, "Apparent Molar Volumes and Temperatures of Maximum Density of Dilute Aqueous Sucrose Solutions," *J. Phys. Chem.*, **74**, 363 (1970).

Green, D. W., Editor *Perry's Chemical Engineers' Handbook*, 6th Ed., McGraw-Hill, New York (1984).

Kaulgud, M. V., and S. S. Dhondge, "Apparent Molal Volumes and Apparent Molal Compressibilities of Some Carbohydrates in Dilute Aqueous Solutions at Different Temperatures," *Indian J. Chem.*, **27A**, 6 (1988).

Kell, G. S., "Density, Thermal Expansivity, and Compressibility of Liquid Water from 0° to 150°C: Correlations and Tables for Atmospheric Pressure and Saturation Reviewed and Expressed on 1968 Temperature Scale," *J. Chem. Eng. Data*, **20**, 97 (1975).

Kiyosawa, K., "The Volumes of Hydrated Glucose, Sucrose and Raffinose Molecules, and the Osmotic Pressures of these Aqueous Saccharide Solutions as Measured by the Freezing-Point Depression Method," *Bull. Chem. Soc. Jap.*, **61**, 633 (1988).

Levin, R. L., "The Freezing of Finite Domain Aqueous Solutions: Solute Redistribution," *Int. J. Heat Mass Trans.*, **24**, 1443 (1981).

Millero, F. J., "The Apparent and Partial Molal Volume of Aqueous Sodium Chloride Solutions at Various Temperatures," *J. Phys. Chem.*, **74**, 356 (1970).

Munson, C. L., "Thermodynamic Studies of the Absorption Freezing Vapor Compression Process," MS Thesis, University of Delaware (1980).

Omran, A. M., and C. J. King, "Kinetics of Ice Crystallization in Sugar Solutions and Fruit Juices," *AIChE J.*, **20**, 795 (1974).

Picker, P., E. Tremblay, and C. Jolicouer, "A High-Precision Digital Readout Flow Densimeter for Liquids," *J. Sol. Chem.*, **3**, 377 (1974).

Wagenbreth, H., H. Toth, and A. Kozdon, "Neue Messungen der Dichte wassriger Saccharoseloeseungen," *PTB-Mitteilungen*, **98**(3) 198 (1988).

Weast, R. C., Editor *CRC Handbook of Chemistry and Physics*, CRC Press, Inc., Boca Raton, FL (1987).